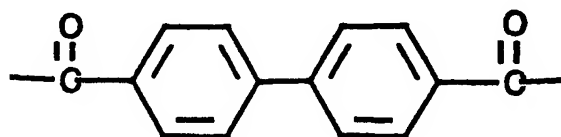




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>B32B 5/16</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 94/13467</b> <b>(43) International Publication Date:</b> 23 June 1994 (23.06.94)
<b>(21) International Application Number:</b> PCT/US92/10700 <b>(22) International Filing Date:</b> 9 December 1992 (09.12.92)  <b>(71) Applicants (for all designated States except US):</b> HOECHST AKTIENGESELLSCHAFT [DE/DE]; Postfach 800 320, D-6320 Frankfurt am Main 80 (DE). HOECHST CELANESE CORPORATION [US/US]; Route 202-206 North, Somerville, NJ 08876 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> BENNETT, Cynthia [US/DE]; Mainstrasse 22, D-6200 Wiesbaden (DE). CHOE, E-Won [US/US]; 130 Radtke Road, Randolph, NJ 07869 (US). FLINT, John, Anthony [GB/US]; 150 Lenape Lane, Berkeley Heights, NJ 07922 (US). KUHMAN, Bodo [DE/DE]; Lindenstrasse 5, D-6258 Runkel 5 (DE).  <b>(74) Agents:</b> CLEMENTS, Gregory, N. et al.; Hoechst Celanese Corporation, 4000 Barclay Downs Drive, Patent Dept., Charlotte, NC 28232-2414 (US).		<b>(81) Designated States:</b> CA, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** BIAXIALLY ORIENTED PENBB FILM PRIMED WITH RADIATION CURABLE COATING COMPOSITION



(I)

**(57) Abstract**

The instant invention deals with abrasion resistant coated, biaxially oriented self-supporting copolyester film, wherein the copolyester is PENBB and wherein the abrasion resistant, cured coating is derived from an aqueous silica/silanol dispersion and one or more acrylate or methacrylate monomers. PENBB is a copolyester containing units of formula (I).

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

## BIAXIALLY ORIENTED PENBB FILM PRIMED WITH RADIATION CURABLE COATING COMPOSITION

### Background of the Invention

5           The present invention relates to an abrasion-resistant synthetic film comprising a biaxially oriented PENBB film and a cured coating composition thereon.

          Polyethylene terephthalate (PET) films have recently found expanded applications as transparent and translucent layers applied to solid substrates and especially to transparent substrates. Thus, such films may be applied to  
10           windows and viewing or lighting media to control the transparency thereof. Additionally, PET films have found many varied applications as independent substrates including uses in the optical arts for display purposes and in conjunction with electronic equipment having visual or optical screens and/or  
15           overlays. Also, recently developed membrane touch switches may contain an outer layer of PET film. An extremely important application is the automotive windshield (laminated safety glass) market.

          While PET films have been used in these applications, tensile strength, stiffness (tensile modulus), improved barrier properties, heat stability, moisture adsorption, UV resistance, shrinkage and abrasion resistance of such films  
20           still require improvement to maximize the durability of the films in further processing and use. Prior artisans have suggested coating PET and other films with a wide variety of scratch-resistant coatings, including coatings containing one or more polyorganosiloxane compounds.

25           Many of the previous proposals to improve abrasion-resistance have involved an aqueous dispersion of silica and at least one polyorganosiloxane which is applied to a synthetic substrate, such as PET, and then thermally cured. For example, R. Ubersax, "Coated Polymeric Substrates," U.S. Pat. No. 4,177,315 discloses an abrasion resistant coating composition comprising from about 5 to 50 weight percent solids comprising from about 10  
30           to 70 weight percent silica and about 90 to 30 weight percent of a partially polymerized organic silanol of the general formula  $\text{RSi}(\text{OH})_3$ , wherein R is

selected from methyl and up to about 40% of a radical selected from the group consisting of vinyl, phenyl,  $\gamma$ -glycidoxy-propyl, and  $\gamma$ -methacryloxypropyl, and about from 95 to 50 weight percent solvent, the solvent comprising about from 10 to 90 weight percent water and about from 90 to 10 weight percent lower aliphatic alcohol, the coating composition having a pH of greater than about 6.0 and less than about 8.0. The above described coating composition is applied to the PET substrate and subsequently cured at a temperature of from 20° to 150°C, preferably from 100° to 150°C. Curing catalysts such as alkali-metal salts of carboxylic acids and quaternary ammonium carboxylates can be included in the coating composition.

Another example is D. Olson et al, "Abrasion Resistant Silicone Coated Polycarbonate Article," U.S. Pat. No. 4,239,798 which discloses a polycarbonate substrate primed with a thermoplastic acrylic polymer which is subsequently coated with a thermoset, silica-filled, organopolysiloxane top coat. This top coat is the condensation product of a silanol of the formula  $\text{RSi}(\text{OH})_3$  in which R is selected from the group consisting of alkyl radicals of 1 to 3 carbon atoms, the vinyl radical, the 3,3,3-trifluoropropyl radical, the  $\gamma$ -glycidoxypropyl radical and the  $\gamma$ -methacryloxypropyl radical, at least 70 weight percent of the silanol being  $\text{CH}_3\text{Si}(\text{OH})_3$ .

A number of patents teach the use of an abrasion resistant coating comprising a dispersion of colloidal silica in an aliphatic alcohol/water solution of the partial condensate of an alkyltrialkoxysilane, which must be primarily methyl trimethoxysilane. In these inventions the abrasion resistance of the coating is typically improved by incorporation of an additional component. A representative example is U.S. Pat. No. 4,277,287 which teaches the inclusion of a small amount of a polysiloxane polyester copolymer. Other patents which may be included within this group are U.S. Pat. Nos. 4,474,857; 4,436,851; 4,413,088; 4,373,061; 4,368,241; 4,368,236; 4,368,235; 4,367,262; 4,298,655; and 3,985,997.

There are a few patents which teach the use of radiation curable polysiloxane-based abrasion-resistant coatings. For example, V. Cross, "Polyester Film Having Abrasion Resistant Radiation Curable Silicone Coa-

ting," U.S. Pat. No. 4,310,600 teaches a coating composition comprising a silica/silanol composition being derived from a composition comprising a dispersion of colloidal silica in a lower aliphatic alcohol-water solution of the partial condensate of a silanol of the formula  $\text{RSi(OH)}_3$ , in which R is selected from the group consisting of unsubstituted and inertly substituted alkyl radicals having one to three carbon atoms and unsubstituted and inertly substituted phenyl radicals, at least about 70 weight percent of said silanol being of the above formula wherein R is  $\text{CH}_3$ , said silica/silanol composition containing about 10 to about 70 weight percent of said colloidal silica and about 30 to about 90 weight percent of said partial condensate, based on the total solids weight; and one or more multifunctional acrylate monomers and/or oligomers; and optionally one or more photoinitiators.

Similarly, R. Chung, "Abrasion Resistant Ultraviolet Light Curable Hard Coating Compositions," U.S. Pat. No. 4,348,462 discloses a radiation curable coating composition which comprises (a) colloidal silica, (b) acryloxy or glycidoxy functional silanes, (c) non-silyl acrylates and (d) catalytic amounts of UV sensitive cationic and radical type photoinitiators. Other patents which disclose UV curable polyorganosiloxane coating compositions include U.S. Pat. Nos. 4,595,471 and 4,571,349.

20

#### Brief Summary of the Invention

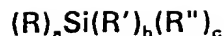
It has now been found that an abrasion resistant coated self-supporting biaxially oriented copolyester film, wherein the copolyester is PENBB and wherein the abrasion resistant coating is derived from a radiation curable coating composition comprising an aqueous silica/silanol dispersion in combination with one or more acrylate or methacrylate monomers provides excellent heat stability, improved tensile strength and stiffness (tensile modulus), improved barrier properties, lower moisture adsorption, higher UV resistance and lower shrinkage while providing improved abrasion resistance.

30

Preferably, the coating composition comprises:

(a) colloidal silica and the partial condensate of a silane, such that at least 60 percent of the silane is a vinyl-functional silane conforming to the

formula



wherein

R is allyl or vinyl functional alkyl

5 R' is hydrolyzable alkoxy, phenoxy or alkyl carbonyloxy

R'' is non-hydrolyzable, saturated alkyl, phenyl, or siloxy such that  
 $a + b + c = 4$ ; and  $a \geq 1$ ;  $b \geq 1$ ;  $c \geq 0$ ,

(b) one or more multifunctional acrylate or methacrylate monomers.

Most of these coatings are disclosed in U.S. Patent No. 4,822,828 for PET  
 10 film.

U.S. Patent No. 3,008,934 discloses copolyesters containing as acid  
 derived units 4,4'-bibenzoate and a host of other dicarboxylates including  
 2,6-naphthalic dicarboxylate. It also discloses oriented fibers and films prepa-  
 red from these copolyesters, however, biaxially oriented PENBB films are not  
 15 disclosed or envisioned. In particular, those films with improved stiffness  
 (tensile modulus) and tensile strength in both MD and TD as well as thermo-  
 stability, UV stability, hydrophobicity, dimensional stability and impermeability  
 toward gases in comparison to PET film are not disclosed in U.S. Patent No.  
 3,008,934.

20 In a preferred embodiment, the present invention relates to a primed  
 biaxially oriented PENBB film having an abrasion resistant layer over a primer  
 layer, said abrasion resistant layer comprising the crosslinked reaction product  
 of a radiation curable coating composition comprising:

(i) colloidal silica and the partial condensate of silane, such that at least  
 25 60 % of the silane is a vinyl-functional silane of the formula



wherein

R is allyl or vinyl functional alkyl

30 R' is hydrolyzable alkoxy, phenoxy or alkyl carbonyloxy

R'' is a non-hydrolyzable, saturated alkyl, phenyl, or siloxy such that  $a + b + c = 4$ ; and

- (ii) one or more multifunctional acrylate or methacrylate monomers; and
- (iii) optionally, one or more photoinitiators.

In a most general aspect, the present invention relates to an abrasion-resistant, biaxially oriented PENBB film prepared by melt extruding a PENBB resin in sheet-like form and cooling said resin to produce a substantially amorphous cast PENBB sheet, orienting said cast PENBB sheet in one direction, thereby producing a uniaxially oriented PENBB film, coating said uniaxially oriented PENBB film with an adhesion-promoting primer composition, thereby producing coated PENBB film, orienting said coated PENBB film in a direction perpendicular to the first direction of orientation, thereby producing biaxially oriented PENBB film, heatsetting said biaxially oriented PENBB film, coating said biaxially oriented PENBB film with a silica/silanol dispersion containing one or more acrylates or methacrylate monomers, drying said coating, and curing said coating by irradiation.

In a preferred aspect, the invention relates to an abrasion resistant biaxially oriented PENBB film prepared as described above, wherein the radiation curable coating composition comprises:

- (i) a dispersion of colloidal silica in a lower aliphatic alcohol/water solution together with the partial condensate of a silane, such that at least 60 weight percent of the silane is a vinyl-functional silane of the formula



wherein

R is allyl or vinyl functional alkyl

R is hydrolyzable alkoxy, phenoxy or alkyl carbonyloxy

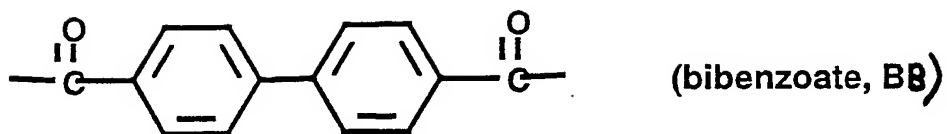
R'' is non-hydrolyzable, saturated alkyl, phenyl, or siloxy such that  $a + b + c = 4$ ; and

- (ii) one or more multifunctional acrylate or methacrylate monomers; and
- (iii) optionally one or more photoinitiators.

#### Detailed description of the invention

PENBB as mentioned hereinbefore is a copolyester containing as acid-derived unit at least 5 mole percent of a radical of the formula

6



In the case that more than 10 mole percent of terephthalic acid derived radicals are present in the copolymer, the content of bibenzoate derived units is at least 25 mole percent. Films of these copolyesters are mentioned in the unpublished German Patent Application P 4224161.8, which is incorporated  
5 herein by reference.

Preferably PENBB is a copolyester wherein at least 80 mole percent of the acid derived units (NBB) consist of bibenzoate (20 to 80 mole percent, preferably 40 to 60 mole percent). The remaining 20 or less mole percent  
10 may consist of other acid derived units, which e.g. affect the melting point or the crystallization kinetics. Preferably at least 80 mole percent of the diol-derived units consist of - O(CH<sub>2</sub>)<sub>2</sub>-O-units. The remaining 20 or less mole percent consist of other diol-derived units, which e.g. may also affect the melting point or the crystallization kinetics. It may also be desirable to  
15 replace minor amounts of the acid- and/or diol-derived units with hydroxycarboxylic-acid-derived units, e.g. such derived from p-hydroxybenzoic acid. In order to achieve the desired mechanical properties in the biaxially oriented PENBB film it is recommended that the IV value (inherent viscosity, as measured in a 1 : 1 weight-ratio mixture of pentafluorophenol and hexafluoroisopropanol at a concentration of 0.2 g/dl and a temperature of 25 °C) of the  
20 PENBB polymer after extrusion be > 0.5 dl/g and preferably > 0.55 dl/g.

To produce the film, the polymer melt is extruded through a die onto a chill roll where it solidifies, is then biaxially oriented, heat set, optionally post treated and wound on a roll. The solidified film as extruded on the chill  
25 roll should be obtained in an essentially amorphous state. To achieve this, the melt film must be pinned to the chill roll by a known method such as electrostatic pinning or vacuum, air knife or the like.

The biaxial orientation of the film is achieved by stretching the film at elevated temperature in the machine (MD) and transverse direction (TD). This



stretching can be either simultaneous or sequential. In the case of sequential stretching the first stretching step can be in either MD or TD, followed by stretching in the other direction. The orientation in MD can also be achieved in several steps, either one after another prior to stretching in TD, or before and after the TD stretching. Preferred temperatures for stretching lie between the glass transition temperature and about 30°C above the cold crystallization temperature of the PENBB copolymer composition in use (both temperatures can easily be measured on amorphous films by DSC). The total stretch ratios ( $\lambda$ ) in MD and TD lie between 1 : 2 and 1 : 10, preferably between 1 : 2.5 and 1 : 5. The product of the total stretch ratios should be between 1 to 30 preferably between 5 to 20. Biaxial drawing is performed such that the birefringence is  $< 0.2$ , preferably  $< 0.1$  to ensure adequately isotropic properties. Birefringence as mentioned herein is the absolute value of the difference between the maximum and minimum refractive indices in the plane of the film, as measured on common instruments such as Abbé refractometer, optical bench or compensators.

In order to optimize properties, relaxation steps can be included in the orientation and heat setting processes.

The heat setting takes place at a temperature between the cold crystallization temperature and the melt temperature of the copolymer composition.

Prior to coating the PENBB film surface with the abrasion resistant coating composition, the film may be surface treated in a conventional manner by exposure to, e.g. an electric corona discharge, plasma or flame treatment. Electric corona discharge is a conventional surface treatment which is commonly performed on a film to enhance the film surface qualities. Electric corona discharge methods and apparatus are described in the U.S. Patent Nos. 3,057,792 and 4,239,973. For biaxially oriented film, the corona treatment followed by the acrylic polymer coating may occur during the in-line manufacturing process, either before stretch orientation, or between the machine draw and transverse draw of biaxial stretch orientation, or after stretch orientation. If the corona treatment and coating steps occur after stretch orientation, it is necessary to completely dry the film before winding.

If the corona treatment and coating occur before orientation, or between draw during orientation, the later orientation steps which require the film to be heated would dry off the excess water from the acrylic polymer coating. Preferably, for biaxially oriented PENBB film the corona treatment and subsequent acrylic polymer coating occur between the draws during the stretch orientation step.

The PENBB film is coated on the surface treated side preferably with an aqueous dispersion of the abrasion resistant coating composition described below. The coating composition may conveniently be applied as an aqueous dispersion using any of the well known coating techniques. For example, the film may be coated by roller coating, spray coating, gravure coating, or slot coating. The heat applied to the film during the subsequent pre-heating, stretching, and heat setting stages is generally sufficient to evaporate the water, which comprises a portion of the abrasion resistant coating composition.

The coated, biaxially oriented PENBB film may then be heat treated for a period of time necessary to crystallize the film. Crystallization further improves dimensional stability and tensile properties of the biaxially oriented PENBB film. The so coated crystallized, biaxially oriented PENBB film is then wound onto a roll.

Adhesion promoting primers believed suitable for use in the present invention include crosslinkable acrylics, crosslinkable polyester, and amorphous polyester. Crosslinkable acrylics are particularly preferred.

The primer coating is preferably applied to the film after it has been uniaxially stretched but prior to the second stretching operation. Most preferably, the primer coating is applied as a latex after the film has been stretched in the longitudinal direction ("machine direction") and prior to transverse stretching. The latex is preferably thermally cured to form a crosslinked adhesion promoting layer during further processing of the film (i.e. heat-setting).

One acrylic latex having particular utility as a primer coating for PENBB film contains a crosslinkable methyl methacrylate/ethyl acrylate/methacrylami-

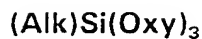
de terpolymer having a molar ratio of about 52.5 : 45.5 : 2. The terpolymer may be present in a concentration ranging from about 0.2 percent to about 45 percent by weight, based on the total weight of the latex coating. Preferably, the terpolymer concentration range is from about 0.4 percent to about 10 percent by weight based on the total weight of the latex coating. In a more preferred embodiment of the instant invention, the terpolymer is present in a concentration of between about 1 percent and about 5 percent by weight, based on the total weight of latex coating. The terpolymer is further characterized by a glass transition temperature in the range of about 40°C to about 50°C. The glass transition temperature of the terpolymer is desirably in the range of between about 43°C and 47°C, and most preferably, the glass transition temperature is about 45°C. In preferred embodiments, the latex coating includes an alkylated melamine formaldehyde cross-linking agent. Of these, hexamethoxymethyl melamine is preferred. The cross-linking agent is generally used in an amount of about 5 percent to about 30 percent, based on the weight of the total solids, and most preferably, about 15 percent to about 25 percent based on the weight of the total solids.

In general, the acrylic primer layer may be at least about 1 nm thick. Desirably, it is about 10 to about 500 nm thick and preferably it is about 10 to about 50 nm thick.

One or more layers of the acrylic primer coating may be applied sequentially to either one or both sides of the PENBB film and the coating latex may include additional additives, as desired.

The abrasion resistant layer is produced by coating a radiation curable coating composition upon the cured acrylic primer layer, removing the solvent, and subsequently crosslinking the coating composition by ultraviolet or electron beam irradiation. As described more fully below, the radiation curable coating comprises an aqueous silica/silanol dispersion in combination with one or more multifunctional acrylate or methacrylate monomers and optionally a photoinitiator.

In the most general aspect, the silanol comprises a compound of the formula:



wherein

Alk is C<sub>1</sub>-C<sub>6</sub> alkyl, and

Oxy is OH, C<sub>1</sub>-C<sub>6</sub> alkoxy

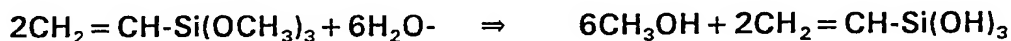
5 Preferably, the silanol is trihydroxymethylsilane.

It is even more preferred to employ a vinyl-functional silanol.

Such a silica/silanol dispersion makes up from 50 to 85, preferably 50 to 60, weight percent of the non-aqueous content of the abrasion resistant coating dispersion. The dispersion is formed by adding an alkoxy silane to  
10 acidic colloidal silica.

Colloidal silica (i.e. small particles of silica suspended in water) is commercially available in both acidic and basic form. The present invention preferably employs acidic (pH of from 3.0 to 5.0) colloidal silica rather than basic suspensions due to stability and solubility considerations. Alternatively,  
15 a basic colloidal silica may be used if the pH is subsequently adjusted to between 3.0 and 5.0 before the addition of the silane.

The preferably employed vinyl-functional silane is hydrolyzed to the corresponding vinyl-functional silanol when it is added to the aqueous suspension of silica. The hydrolysis of vinyltrimethoxysilane is set forth below  
20 as an illustration:



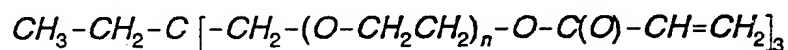
The vinyl-functional silanol then undergoes a "partial" condensation  
25 reaction (with the elimination of water), which has a pH dependent equilibrium. Only partial condensation is desired since driving the reaction to completion will result in solidification of the silanol or "gelling", as well as viscosity problems.

The addition of the silane to the colloidal silica is preferably performed  
30 slowly and with gentle stirring while the silica suspension is at an elevated temperature.

The multifunctional acrylate or methacrylate monomer which forms part of the abrasion resistant coating composition comprises 15 percent to 50 percent, preferably 15 percent to 25 percent, of the coating composition.

The specific acrylate or methacrylate monomer employed in the abrasion resistant coating is not believed critical to the present invention. Any multifunctional acrylate may be employed as long as the specific acrylate monomer selected does not create stability ("gelling") or viscosity problems. Triacrylates are preferred. Water-soluble triacrylates are even more preferred due to lower initial haze.

A non-exhaustive list of multifunctional acrylates believed useful in the present invention includes dipentaerythritol monohydroxypentacrylate; trimethylolpropane triacrylate; pentaerythritol triacrylate; ethoxylated trimethylolpropane triacrylate; ditrimethylolpropane triacrylate; 1,3-butanediol diacrylate; diethylene glycol diacrylate; 1,6-hexanediol diacrylate; neopentyl glycol diacrylate; tetraethylene glycol diacrylate; triethylene glycol diacrylate; tetrahydrofurfural diacrylate; pentaethoxylated Bisphenol A diacrylate; and blends thereof. A highly ethoxylated trimethylolpropane triacrylate, commercially available from Arco Specialty Chemicals under the trademark SARTOMER C-9035, is preferred. This triacrylate is believed to conform to the following structure:



wherein n averages 5 and the degree of ethoxylation for each ethoxylated acrylate segment may be the same or different.

Another preferred acrylate is dipentaerythritol monohydroxypentacrylate, which is commercially available from Arco Specialty Chemicals under the trademark SARTOMER C-9041.

Up to 35 weight percent, preferably 15 to 25 weight percent, based on the total weight of the aqueous dispersion, of a lower aliphatic alcohol may optionally be added to enhance the stability of the silica/partial condensate

dispersion. About 19 weight percent of isopropanol is preferred as the lower aliphatic alcohol.

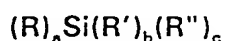
If the radiation curable coating is to be crosslinked by electron beam irradiation, no photoinitiator is required to initiate or catalyze the reaction. If  
 5 an ultraviolet radiation source is used to crosslink the coating composition, then the inclusion of a photoinitiator compound into the coating composition is necessary. The photoinitiator, if one is employed, comprises up to 10 percent of the composition, preferably 1 to 3 percent.

A non-exhaustive list of photoinitiators believed useful in the present  
 10 invention includes benzophenone, hydroxycyclohexylphenylketone, acetophenone, acenaphthenequinone, o-methoxy benzophenone, thioxanthen-9-one, xanthen-9-one, 7H-benz[d,e]anthracen-7-one, dibenzosuberone, 1-naphthaldehyde, 4,4'-bis-(dimethylamino)-benzophenone, fluorene-9-one, 1-acetona-  
 15 phthanthene anthraquinone, 1-indanone, 2-t-butyl anthraquinone, valerophenone, hexanophenone, 3-phenylbutyrophenone, p-morpholinopropiophenone, 4-morpholinobenzophenone, p-diacetyl-benzene, 4-amino-benzophenone, 4-methoxyacetophenone, benzaldehyde, 9-acetylphenanthrene, 2-acetylphenanthrene, 10-thioxanthenone, 3-acetylphenanthrene, 3-acetylindole, 1,3,5-triacetylbenzene and the like, including blends thereof. A 50/50 weight  
 20 percent blend of benzophenone and 1-hydroxycyclohexylphenylketone is preferred.

As stated above, a specific organosilane in its radiation curable coating composition is employed. More particularly, it has been found that radiation curable silica/organopolysiloxane coating compositions which preferably  
 25 employ vinyl-functional silanes as the major or primary organosilane possess superior abrasion resistance over these coating compositions which employ methyltrimethoxy-silane as the primary organosilane.

The preferred vinyl-functional silanes which are believed operable in the present invention conform to the formula

30



wherein

R is allyl or vinyl-functional alkyl

R' is hydrolyzable alkoxy, phenoxy, or alkylcarbonyloxy

R" is non-hydrolyzable, saturated alkyl, phenyl, or siloxy such that  
5  $a + b + c = 4$ ; and  $a \geq 1$ ;  $b \geq 1$ ;  $c \geq 0$ .

The term "allyl or vinyl-functional alkyl" means any radical having at least one allyl or vinyl group. In particular the term "allyl or vinyl-functional alkyl" means an allyl or vinyl group which is optionally mono- or polysubstituted with one or more identical or different radicals from the group consisting of C<sub>1</sub>-C<sub>3</sub> alkyl, Cl-, F-, Br-, CF<sub>3</sub>, NO<sub>2</sub> and CN.  
10

By "hydrolyzable alkoxy, phenoxy or alkyl carbonyloxy" it is meant any alkoxy, phenoxy or alkyl carbonyloxy substituent which will be readily hydrolyzed when the vinyl-functional silane is added to the colloidal silica as described above and which will not impart undesirable haze to the cured abrasion resistant layer. C<sub>1</sub>-C<sub>3</sub> alkoxy groups, such as methoxy, ethoxy, and propyloxy, come within this definition, with methoxy being preferred. C<sub>1</sub>-C<sub>6</sub> alkyl carbonyloxy groups are preferred, such as acetoxyl.  
15

A "non-hydrolyzable saturated alkyl" is a C<sub>1</sub>-C<sub>6</sub> alkyl group, preferably a C<sub>1</sub>-C<sub>3</sub> alkyl group with methyl being especially preferred. The "non-hydrolyzable phenyl" may be unsubstituted or mono- or up to penta-substituted with one or more identical or different substituents selected from the group consisting of C<sub>1</sub>-C<sub>3</sub> alkyl, F, Cl, Br, CF<sub>3</sub>, NO<sub>2</sub> and CN.  
20

The "non-hydrolyzable siloxy" is a tri-lower alkyl siloxy group with lower alkyl being C<sub>1</sub>-C<sub>3</sub> alkyl. The preferred non-hydrolyzable siloxy group is triethoxy siloxy.  
25

The following vinyl-functional silanes satisfy the above formula: vinyltris(2-methoxyethoxy)silane, vinyl-triethoxysilane, vinyltriisopropenoxysilane, phenylvinyl-diethoxysilane, vinyltris(t-butylperoxy)silane, vinylmethyldiethoxysilane, vinyltris-t-butoxysilane, vinyl-dimethylethoxysilane, vinyltriphenoxysilane, diphenylvinylethoxysilane, vinyltrimethoxysilane, 1,3-divinyltetraethoxydisiloxane, and vinyltriisopropoxysilane.  
30

The preferred vinyl-functional silanes include vinyltriethoxysilane, vinyltrimethoxysilane and vinyltris(2-methoxyethoxy)silane, with vinyltrimethoxysilane being most preferred.

5 The radiation curable coating composition may be applied to the PENBB film by any convenient method, including spray coating, gravure coating, and slot coating techniques.

In general, the radiation curable coating is at least about 1  $\mu\text{m}$  thick. Desirably, it is at least about 5  $\mu\text{m}$  thick and is preferably about 6 to about 10  $\mu\text{m}$  thick.

10 The dispersion solvent should be substantially removed from the surface of the coated PENBB film prior to curing the vinyl-functional organopolysiloxane. Solvent removal may be accomplished by drying the coated film at temperatures ranging from 75° to 150° C for a time sufficient to evaporate the water or water/lower aliphatic alcohol solvent system.

15 The dried radiation curable coating may be conveniently cured by electron beam or ultraviolet irradiation. Ultraviolet irradiation is preferred.

The abrasion resistant biaxially oriented PENBB film of the present invention has utility in the field of multilayer automotive windshields. While various laminates and constructions are known, such windshields typically  
20 comprise at least one layer of polyvinylbutyral sandwiched between two sheets of glass. More recently, U.S. Pat., No. 4,242,403 disclosed bonding a second layer of polyvinylbutyral to the exposed surface of the "inside" glass sheet and overlaying the second polyvinylbutyral layer with an abrasion resistant synthetic film. The abrasion resistant film comprises polyester  
25 which has a fully cured, silica reinforced methylsiloxane coating on its exposed surface. The disclosure of U.S. Pat. No. 4,242,403 in its entirety is hereby incorporated by reference.

Yet another application of this invention is in the field of window glazing. The abrasion resistant biaxially oriented PENBB film is laminated to  
30 a sheet of glass.



Another application of this invention is in the field of touch panels where the abrasion of the film must be reduced for usage, i.e. membrane switch face plates.

Another application of this invention is in the field of backside printed labels and packaging, where clarity to the underlying information is required.

Another application of this invention is in the field of magnetic coated tape where the abrasion resistant coating would reduce the wear of the tape running through the tape machine.

10

## EXAMPLES

The following Examples are intended to more fully illustrate the practice and advantages of the present invention. In no event should the specific embodiments recited hereinbelow be construed as explicit or implicit limitations on the generic invention described above.

15

### EXAMPLE I

#### Preparation of the Silica/Vinyl-Functional Silane Dispersion and the Radiation Curable Coating:

48.0 g of vinyltrimethoxysilane are added dropwise at room temperature to 72 g of Nalco 1034A, a commercially available acidic colloidal silica, with gentle stirring using a magnetic stirrer. The mixture is stirred for 4 hours at room temperature in a closed container and then heated to 60°C in a water bath for 30 minutes while still being stirred.

4.8 g of SARTOMER C-9035, a water-soluble, highly ethoxylated trimethylolpropane triacrylate commercially available from ARCO Specialty Chemicals, is mixed with 4.0 g of isopropanol, 0.9 g of IRGACURE 500, a photoinitiator commercially available from Ciba-Geigy, and 0.2 g of a fluorinated surfactant commercially available from 3M under the trademark FC-430. The resulting mixture is added to 12 g of the silica/vinyltrimethoxysilane condensate to form the radiation curable coating composition.

Preparation of an acrylic primed PENBB film

A PENBB film is made from 289 parts by weight of dimethyl 2,6-naphthalene dicarboxylate, 322 parts by weight of dimethyl 4,4'-bibenzoate, and 368 parts by weight of ethylene glycol. Pellets of this polymer, having  
5 a melting point of 281°C are melted in a single screw extruder at temperatures of 280 to 320°C and extruded through a sheet die onto a cooling roll, which is temperature controlled at 20°C. A 120  $\mu\text{m}$  thick film is obtained which is clear and transparent. Its density is 1.31 g/cm<sup>3</sup>. This pre-film is then sequentially biaxially oriented. The longitudinally drawn film is corona  
10 treated by a corona discharge apparatus and thereafter coated with the latex comprised of 4.5 wt-% solids of a copolymer of 60 wt-% methylmethacrylate, 35 wt-% ethylacrylate and 5 wt-% of N-methylolacrylamid and a surfactant by reverse gravure coating. The corona treated longitudinally drawn, coated film is dried at a temperature of about 100°C. Thereafter the  
15 film is stretched in the transverse direction. The biaxially drawn film is heat set at a temperature of 250°C. These heat treatments result in the cross-linking of the primer coating.

Preparation of the final coated biaxially oriented PENBB film

20 The silica/vinyl functional silane coating composition is applied to the acrylic primed PENBB film using a # 18 Meyer rod. The coating is first dried in an oven maintained at 75 °C for one minute and then crosslinked by UV radiation by passing the coated PENBB film four times through a RPC Equipment Co. Model QC 1202 processor at 7.5 m/min using two 80 watt/cm  
25 lamps.

The thus obtained abrasion resistant coated biaxially oriented PENBB film shows the following characteristics compared to a similarly coated PET film. The mechanical properties are measured in a tensile testing machine made by Zwick (Ulm, Germany) on 15 mm wide strips of film. The initial  
30 distance between the chucks is 100 mm and the crosshead speed is 100 mm/min for the strength and elongation determination and 10 mm/min for the tensile modulus determination. The UV resistance is tested by measuring the

retention of tensile elongation after exposure to UV light in a "Suntest" apparatus manufactured by Heraeus (Hanau, Germany) for 14 days.

**TABLE 1**

Property	Units	PENBB	PET
Tensile Strength MD TD	(MPa)	240 180	}100-200
Elongation at Break MD TD	(%)	25 20	}50
Tensile Modulus MD TD	(GPa)	9.2	}4-6
UV resistance	(%) retained tensile strength	77	0
Shrinkage (at 150°C for 15 minutes) MD TD	(%)	0.3 0.3	> 1.0 > 1.0

As is evident from the above table, tensile strength, elongation at break, stiffness (tensile modulus), shrinkage and UV stability are improved as compared to similarly coated PET films.

That which is claimed is:

1. Abrasion resistant coated, biaxially oriented self-supporting copolyester film, wherein the copolyester is PENBB and wherein the abrasion resistant, cured coating is derived from an aqueous silica/silanol dispersion and one or more acrylate or methacrylate monomers.

2. Abrasion resistant coated film according to claim 1, wherein the silanol is a compound according to the formula

$$(Alk)Si(Oxy)_3$$

wherein

Alk is C<sub>1</sub>-C<sub>6</sub>-alkyl and

Oxy is OH or C<sub>1</sub>-C<sub>3</sub>-alkoxy.

3. Abrasion resistant coated film according to claim 1, wherein the abrasion resistant cured coating is derived from a composition comprising colloidal silica and as the silanol a partial condensate of a silane, such that at least 60 percent of the silane is a vinyl-functional silane conforming to the formula



wherein

R is allyl or vinyl-functional alkyl

R' is hydrolyzable alkoxy, phenoxy or alkyl carbonyloxy

R'' is non-hydrolyzable, saturated alkyl, phenyl, or siloxy such that  $a + b + c = 4$ ; and  $a \geq 1$ ;  $b \geq 1$ ;  $c \geq 0$ .

4. An abrasion resistant coated film according to claim 3, wherein the composition further comprises up to 10 percent of a photoinitiator.

5. An abrasion resistant coated film according to claim 3 or 4, wherein said vinyl-functional silane is selected from the group consisting of vinyltris(2-methoxyethoxy)silane, vinyltriethoxysilane, vinyltriisopropenoxysilane, phenylvinyl-diethoxysilane, vinyltris(t-butylperoxy)silane, vinyl-methyldiethoxysilane, vinyltris-t-butoxysilane, vinyl-dimethylethoxysilane, vinyltriphenoxysilane, diphenylvinylethoxysilane, vinyltrimethoxysilane, 1,3-divinyltetraethoxydisiloxane, and vinyltriisopropoxysilane.
6. An abrasion resistant coated film according to any one or more of claims 3, 4 and 5, wherein the composition comprises from 50 to 85 wt-% of the colloidal silica and the partial condensate of the silane and from 15 to 50 wt-% of the acrylate and/or methacrylate monomers.
7. An abrasion resistant coated film according to any one or more of claims 4, 5 and 6, wherein said photoinitiator is a blend of benzophenone and 1-hydroxycyclohexylphenylketone.
8. An abrasion resistant coated film according to any one or more of claims 3 to 7, wherein the composition further comprises from 1 to 35 weight percent, based upon the total weight of the composition, of at least one water soluble alkanol.
9. An abrasion resistant coated film according to claim 8, wherein said water soluble alkanol comprises isopropanol in an amount ranging from 15 to 25 weight percent, based on the total weight of the composition.
10. An abrasion resistant coated film according to any one or more of claims 1 to 9, wherein the birefringence of the PENBB film is  $< 0.2$ .
11. An abrasion resistant coated film according to any one or more of claims 1 to 10, wherein the IV-value of the PENBB polymer is  $> 0.5$  dl/g.

12. Use of the abrasion resistant coated film according to any one or more of claims 1-11 in the production of automotive windshields.

5 13. Use of the abrasion resistant coated film according to any one or more of claims 1-11 in the field of window glazing.

14. Use of the abrasion resistant coated film according to any one or more of claims 1-11 as a membrane switch touch panel.

10 15. Use of the abrasion resistant coated film according to any one or more of claims 1-11 as label or packaging material.

15 16. Use of the abrasion resistant coated film according to any one or more of claims 1-11 as a base film for magnetic tapes.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US92/10700**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) :B32B 5/16

US CL :428/483, 910, 323

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/483, 910, 323

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5,126,394 (REVIS ET AL) 30 JUNE 1992. See Abstract.	1-5



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be part of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

23 FEBRUARY 1993

Date of mailing of the international search report

01 APR 1993

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Authorized officer

E. ROLLINS BUFFALOW

Facsimile No. NOT APPLICABLE

Telephone No. (703) 308-2351

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US92/10700

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☒ Claims Nos.: 12-16  
because they relate to subject matter not required to be searched by this Authority, namely:  
  
Claims 12-16 are directed to a Use. This ISA is not required to search "Use" claims not drafted in method terminology. PCT Article 17(2)(a)(i).
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 6-16  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐  
☐

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.



DERWENT-ACC-NO: 1994-217639

DERWENT-WEEK: 199646

*COPYRIGHT 2008 DERWENT INFORMATION LTD*

TITLE: New abrasion resistant coated biaxially oriented self supporting co:polyester with excellent heat stability and improved mechanical properties used in multilayer windshields

INVENTOR: BENNETT C; CHOE E ; CHOE E R ; FLINT J A ; KUHMAN B

PATENT-ASSIGNEE: HOECHST AG[FARH] , HOECHST CELANESE CORP [FARH]

PRIORITY-DATA: 1992WO-US10700 (December 9, 1992)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE
WO 9413467 A1	June 23, 1994	EN
EP 673309 A1	September 27, 1995	EN
EP 673309 A4	December 6, 1995	EN
JP 08504383 W	May 14, 1996	JA

DESIGNATED-STATES: CA JP KR US AT BE CH DE DK ES FR GB GR IE IT  
LU MC NL PT SE DE FR GB IT LU NL

APPLICATION-DATA:



PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
WO1994013467A1	N/A	1992WO-US10700	December 9, 1992
EP 673309A1	N/A	1992WO-US10700	December 9, 1992
JP 08504383W	N/A	1992WO-US10700	December 9, 1992
EP 673309A1	N/A	1993EP-901400	December 9, 1992
JP 08504383W	Based on	1994JP-514082	December 9, 1992

## INT-CL-CURRENT:

TYPE	IPC DATE
CIPP	B32B9/00 20060101
CIPS	B32B17/10 20060101
CIPS	B32B27/36 20060101
CIPS	B32B5/16 20060101
CIPS	C08J7/04 20060101
CIPS	C08L67/00 20060101
CIPS	C08L67/02 20060101
CIPS	C09D4/02 20060101
CIPS	G11B5/73 20060101
CIPS	G11B5/735 20060101
CIPS	G11B5/738 20060101

ABSTRACTED-PUB-NO: WO 9413467 A1

## BASIC-ABSTRACT:

Abrasion resistant coated, biaxially oriented self-supporting copolyester comprises PENBB as the copolyester and an abrasion resistant cured coating derived from aq. silica silanol dispersion and one or more acrylate or methacrylate monomers.



PENBB is a copolyester contg. at least 5 mole.% bibenzoate units of formula (BB). In the case that more than 10 mole.% terephthalic acid derived radicals are present the content of BB units is at least 25 mole.%.

PENBB is pref. a copolyester contg. at least 80 mole.% acid derived units NBB consisting of 20-80 pref. 40-60 mole.% BB and 80-20 pref. 60-40 mole.% naphthalate. The remaining 20 or less mole.% may consist of other acid derived units which e.g. affect the m.pt. or crystallisation kinetics. Pref. at least 80 mole.% diol derived units consist of  $O(CH_2)_2O$  units and the remaining 20 or less mole.% are other diol derived units which e.g. also affect the m.pt. or crystallisation kinetics.

It may also be desirable to replace minor amts. of the acid and/or diol derived units e.g. such derived from p-hydroxybenzoic acid.

USE/ADVANTAGE - The film has excellent heat stability, improved tensile strength and stiffness (tensile modulus), improved barrier properties, lower moisture adsorption, higher UV resistance and lower shrinkage while providing improved abrasion resistance. The film is used in the field of multilayer windshields, or is laminated to a sheet of glass for window glazing. It may also be used in the field of touch panels where the abrasion of the film must be reduced for usage, i.e. membrane switch face plates; backside printed labels and packaging, where clarity of underlying information is required; or magnetic coated tape where the abrasion resistant coating would reduce the wear of the tape running through the tape machine.

TITLE-TERMS: NEW ABRASION RESISTANCE COATING BIAXIAL ORIENT  
SELF SUPPORT CO POLYESTER HEAT STABILISED  
IMPROVE MECHANICAL PROPERTIES MULTILAYER  
WINDSCREEN

DERWENT-CLASS: A23 A94 L01 P73

CPI-CODES: A04-F06E7; A05-E05; A05-E05A; A06-A00E1; A11-B02A; A11-B05; A11-C02C; A12-B04D; A12-R04; A12-S06; A12-T04A; L01-G04B; L01-H05A;

UNLINKED-DERWENT-REGISTRY- ; 0994U  
NUMBERS:



## ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1] 017 ; D01  
D11 D10 D19 D18 D32 D34 D20  
D50 D93 D95 D94; H0011\*R;  
P0839\*R F41 D01 D63; H0293;  
S9999 S1285\*R; S9999 S1387;

Polymer Index [1.2] 017 ; G1467  
G1456 G1445 D01 D63 F41 E00  
E22 D11 D10 D20 D18 D32 D50  
D93; G1467 G1456 G1445 D01  
D63 F41 E00 E28 D11 D10 D19  
D18 D32 D50 D93; G1025  
G0997 D01 D11 D10 D50 D82  
F28 F26 R00822 21; H0033  
H0011; H0293; L9999 L2528  
L2506; L9999 L2197 L2186;  
S9999 S1547 S1536; S9999  
S1387; S9999 S1285\*R;

Polymer Index [1.3] 017 ; ND01;  
ND04; Q9999 Q7658; Q9999  
Q7818\*R; Q9999 Q9289 Q9212;  
K9676\*R; K9529 K9483; B9999  
B4682 B4568; B9999 B4171  
B4091 B3838 B3747; B9999  
B4079 B3930 B3838 B3747;  
B9999 B4080 B3930 B3838  
B3747; B9999 B4615 B4568;  
K9869 K9847 K9790; B9999  
B4864 B4853 B4740; B9999  
B5287 B5276; Q9999 Q7783;  
Q9999 Q8899\*R Q8877 Q8855;  
K9574 K9483; K9687 K9676;  
K9712 K9676; K9698 K9676;  
Q9999 Q8366\*R; N9999 N7147  
N7034 N7023; N9999 N7192  
N7023; N9999 N6780\*R N6655;

Polymer Index [1.4] 017 ; B9999  
B5163 B5152 B4740;

Polymer Index [1.5] 017 ; N9999  
N5812\*R; N9999 N5925 N5914;  
N9999 N6939\*R; N9999



N5970\*R; N9999 N6633 N6611;  
B9999 B5243\*R B4740; B9999  
B4842 B4831 B4740; B9999  
B5492 B5403 B5276; K9427;  
B9999 B5607 B5572;

Polymer Index [2.1] 017 ; G2302  
G2299 G2266 D01 Si 4A; D00  
F20 O\* 6A Si 4A R01694  
107016; G2266\*R D01 Si 4A  
D11 D10 D50 D81 D82 D83 D84  
D85 D86 D87 D88 D89 D90 D91  
D92 D93 F87 F86; P1445\*R F81  
Si; M9999 M2073; L9999 L2391;  
L9999 L2073; H0022 H0011;

Polymer Index [2.2] 017 ; D01  
D12 D10 D11 D19 D18 D31 D32  
D33 D53 D51 D54 D55 D57 D58  
F87 F86 F81 D88 D93 D91 D92  
D85 D94 F41 D63 G0691\*R  
G0022; G2277\*R G2266 D01 Si  
4A; D00 F20 O\* 6A Si 4A  
R01694 107016; P1445\*R F81  
Si; H0022 H0011; L9999 L2391;  
L9999 L2073; M9999 M2073;

Polymer Index [2.3] 017 ; ND01;  
ND04; Q9999 Q7658; Q9999  
Q7818\*R; Q9999 Q9289 Q9212;  
K9676\*R; K9529 K9483; B9999  
B4682 B4568; B9999 B4171  
B4091 B3838 B3747; B9999  
B4079 B3930 B3838 B3747;  
B9999 B4080 B3930 B3838  
B3747; B9999 B4615 B4568;  
K9869 K9847 K9790; B9999  
B4864 B4853 B4740; B9999  
B5287 B5276; Q9999 Q7783;  
Q9999 Q8899\*R Q8877 Q8855;  
K9574 K9483; K9687 K9676;  
K9712 K9676; K9698 K9676;  
Q9999 Q8366\*R; N9999 N7147  
N7034 N7023; N9999 N7192



N7023; N9999 N6780\*R N6655;

Polymer Index [2.4] 017 ; D01  
 D12 D10 D51\*R D63 F41; G0340  
 G0339 G0260 G0022 D01 D11  
 D10 D12 D51 D53 D58 D63 D85  
 F41 R01126 7785; G0384  
 G0339 G0260 G0022 D01 D11  
 D10 D12 D51 D53 D58 D63 D85  
 F41 R00479 7200; G0453  
 G0260 G0022 D01 D11 D10 D12  
 D51 D53 D58 D84 F27 F26 F70  
 R07701 24262; A999 A157\*R;  
 A999 A179 A157; A999 A771;

Polymer Index [2.5] 017 ; D01  
 D14 D13 D19 D18 D32 D50 D93  
 F23 F27 F26; D01 D19 D18 D32  
 D50 D93 F23 R00994 259; A999  
 A771; A999 A179 A157;

#### POLYMER-MULTIPUNCH-CODES-AND-KEY-SERIALS:

Key Serials:

0004

0016

0034

0036

0149

0152

0155

0167

0170

0224



0226

0231

0541

0548

0646

1054

1058

1288

1291

1303

1306

1319

1384

1454

1464

1944

1948

2016

2020

2102



2104

2123

2177

2194

2196

2198

2285

2300

2368

2386

2421

2431

2437

2453

2478

2493

2500

2510

2513

2544



2547

2600

2602

2628

2635

2646

2654

2657

2667

2680

2726

2774

2791

2818

2827

2829

2835

3017

3024

3089



Multipunch Codes:

3225

3237

3240

3255

3267

3317

02&

038

04-

081

143

144

151

155

157

162

163

167

169

170

171



239

28&

331

353

369

381

395

402

408

409

415

42&

431

435

437

443

447

450

452

463



466

467

470

477

494

50&

53&

540

541

551

560

566

567

57&

573

575

581

59&

596

597



598

604

608

610

615

668

669

672

679

727

02&

034

038

04-

05-

074

076

077

079

08&



081

082

083

086

10-

116

17&

17-

19-

20&

225

229

230

231

27&

273

331

341

353

359



38-

381

402

408

409

42&

431

44&

443

473

477

48-

540

541

551

560

566

567

57&

573



597

598

610

615

668

669

672

681

720

727

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: 1994-099000

Non-CPI Secondary Accession Numbers: 1994-171919